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A Carbon-13 NMR Study of Carbon Dioxide Absorption and Desorption with Aqueous Amine Solutions

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Abstract

Quantitative ^{13}C NMR spectroscopy was used to study the reaction of CO_2 with aqueous amines. A number of structurally different amines were studied using this method to investigate their CO_2 absorption and desorption under different reaction conditions. The results demonstrate that this method is easily applicable to both CO_2 absorption and desorption with aqueous amines solutions. The study showed that this technique can be used to investigate the reaction mechanism of amine solvents with CO_2, and also give their absorption and desorption capacities. The easy application of this method to monitor speciation of the amine-H_2O-CO_2 reaction system makes it a useful tool in the development of new amine solvents for post combustion capture (PCC).

Key word: carbon dioxide, amine, absorption, desorption, NMR

1. Introduction

Climate change is receiving significant attention around the world, with many scientists from different fields working on means to efficiently reduce CO_2 emission from human activities, especially from the energy industry. Post combustion capture (PCC) has been demonstrated as a viable process to reduce CO_2 released from fossil fuel based electricity generation. Aqueous amines are very promising materials for use in the PCC process, due to their high capacity for CO_2 absorption at low CO_2 partial pressure and economic affordability. Importantly, this process can be retrofitted to existing power stations or integrated into new ones. There are currently several demonstration pilot plants in operation around the world to study the application of aqueous amines in post combustion CO_2 capture from coal fired power station flue gases [1].

The application of aqueous amines for PCC includes two major reactions, CO_2 absorption and desorption. The total energy input for PCC using monoethanolamine (MEA) as a “solvent” may be as high as 30% of the power

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generated. To make the wide spread application of this technology, commercially viable new amine solvents with lower overall energy requirements must be developed.

The study of speciation in the absorption and desorption processes can provide information about species formation and conversion in the reactions, reveal the relationship between an amine's capacity for CO_2 capture and its chemical structure, and show the influence of reaction conditions on amine behaviors in CO_2 capture. Speciation of amine-H_2O-CO_2 reactions has not been studied thoroughly and only a few papers have been published [2]. In the most recent speciation study of an amine-H_2O-CO_2 system, Boettinger et al. [2] have described their online NMR spectroscopic study of the species distribution in MEA-H_2O-CO_2 and DEA-H_2O-CO_2 systems. This work required a custom experimental apparatus, and analyzed the species formed in the reactions with online ^{1}H and ^{13}C NMR spectroscopy. Hook [3] designed an efficient method to measure CO_2 absorption and desorption in his study of the reaction of sterically hindered aqueous amines with CO_2. He used quantitative ^{13}C NMR spectroscopy to identify species at the end of an absorption and desorption cycle. These results demonstrate that quantitative ^{13}C NMR spectroscopy is an efficient tool for use in the study of the amine-H_2O-CO_2 reaction system. By monitoring speciation in whole CO_2 absorption and desorption processes in an open-ended reaction system, it is possible to reveal relationships between amine structures on the one hand, and reaction mechanism and kinetics, influence of reaction conditions and amine capacities of CO_2 capture on the other. The information and knowledge obtained from this study can be used to improve continuous absorbing-desorbing reaction systems and provide guidelines for new amine solvent development for CO_2 capture using the PCC process.

2. Application of Quantitative ^{13}C NMR and Reaction Apparatus

Aqueous primary and secondary amines react with CO_2 via two major mechanisms: the nucleophilic reaction to generate carbamate derivatives (eq 1) and acid-base neutralization to form bicarbonate compounds (eq 2). The nucleophilic reaction is much faster than the acid-base neutralization according to our observations in this study. Carbamate derivatives formed in this reaction may also generate carbonate/bicarbonate via a hydrolysis at a suitable stage in the reaction (eq 3 and 4). It is apparent that the formation of bicarbonate consumes more CO_2 than the formation of carbamates. Additionally carbamates are thermally more stable than bicarbonates and consume higher energy in the CO_2 desorption process. Tertiary amines do not form carbamates due to the absence of amino-hydrogen atoms, and hence can only undergo acid-base neutralization when they react with CO_2 in aqueous solution (eq 2 where $R_1 \neq H$; $R_2 \neq H$; $R_3 \neq H$). Tertiary amines therefore have potentially higher CO_2 absorbing capacity than primary and secondary amines because they cannot form carbamates; however, they are not an ideal choice for use in PCC as their reaction with CO_2 is slow. The ideal amine solvent to capture CO_2 via PCC should have high speed and high capacity for CO_2 absorption, as well as a high speed, high completion and low energy consumption to release CO_2 in the desorption process. Therefore, a clear picture of the speciation of the amine-H_2O-CO_2 reaction as a function of reaction time can provide a valuable guideline to assist in the design of new amine solvents.

$$R_1R_2NH + CO_2 \rightleftharpoons \left[R_1R_2N\text{-}C(O)\text{-}OH\right] \xrightleftharpoons{R_1R_2NH} R_1R_2N\text{-}C(O)\text{-}O^{\ominus}\ \ {}^{\oplus}NH_2R_1R_2 \qquad \text{(eq 1)}$$

$R_1 \neq H$, $R_2 = H$; $R_1 \neq H$, $R_2 \neq H$;

$$R_1R_2R_3N + CO_2 + H_2O \rightleftharpoons R_1R_2NH_2\,HCO_3 \qquad \text{(eq 2)}$$

$$\left(R_1R_2N\text{-}C(O)\text{-}O^{\ominus}\ \ {}^{\oplus}NH_2R_1R_2\right) + H_2O \rightleftharpoons (R_1R_2NH_2)_2\,CO_3 \qquad \text{(eq 3)}$$

$$(R_1R_2NH_2)_2\,CO_3 + CO_2 + H_2O \rightleftharpoons 2\,R_1R_2NH_2\,HCO_3 \qquad \text{(eq 4)}$$

The main ^{13}C NMR resonances used in this quantitative study are those associated with the carbonyl groups of different species at different reaction times. Integration of these resonances allows us to measure the amount of carbonyl group in solution relative to the total amine amount, and from that to calculate the relative amounts of each species present. This data provides the amount of CO_2 reacted with amines in absorption, or carbonyl groups

remaining in desorption, their speciation, and reaction rates. After the reaction conditions (concentration, temperature, CO_2 partial pressure and flow rate, pH, etc) are standardized, this study will provide information about the relationship between the behaviour of amines in CO_2 absorption and desorption and their chemical structures. Specifically, it will provide us with information on reaction rates, the stability of intermediates and products formed in these reactions, and the reaction mechanism.

In our study samples are taken at different reaction times, sealed, and are analyzed with ^1H and quantitative ^{13}C NMR spectroscopy. The quantitative ^{13}C NMR provides clear speciation information and is useful in the calculation of the mole percentage of each species relative to the total amine concentration. The ^1H NMR data is used as supporting evidence in this study. The NMR relaxation times (T1) of carbon atoms, including carbamates and bicarbonates, are measured, and the delay times (D1) set at $\geq 5\ T1_{max}$ ($T1_{max}$ is the longest T1 of the carbon among all the carbon atoms in the reaction mixture), in order to ensure that the integration of all the carbon atoms is quantitative. In most cases, the carbonyl carbons of carbamates have longer T1 values than that of bicarbonate, and of carbon atoms in amines.

The products and intermediates formed in the amine-H_2O-CO_2 system were stable during this quantitative ^{13}C and ^1H NMR spectroscopy. The samples were taken directly from the reaction solution to a glass NMR tube (5mm) and then sealed with plastic caps. Our investigation showed that MEA bicarbonate was stable during NMR analysis, and MEA carbamate was more stable, decomposing only partially after being heated with an oil bath at 100°C over night. Different aqueous amines also showed excellent stability once sealed.

Some species generated in the amine-H_2O-CO_2 reaction system are sensitive to the pH of the solution, and their proton and/or carbon NMR signals shift while the reaction pH changes. An external standard reference of 1,4-dioxane was therefore added to the NMR tube for analysis. This reference was calibrated with another external reference of trimethylsilane (TMS) in H_2O via an unlocked run and its ^{13}C signal appeared at δ 67.18 ppm.

Absorption reactions were performed in a 50 ml 2-necked pear-shaped flask, with a water condenser topped with a small ice trap. Pure CO_2 gas (99.9%) was bubbled through the amine solution via a Teflon tube (0.028″ x 0.07″), and the flow rate set at 5 ml/min after several trial experiments. This flow rate was selected as it was suitable to our study need, to obtain enough details of fast reaction and to complete slow reactions in a planned time frame. The amine solution was stirred at a speed of 900 rpm with an egg-shaped stirring bar (5/8″ x ¼″). Desorbing reactions were also carried out in the same apparatus, with CO_2 rich aqueous amine solutions obtained from absorption procedure.

3. Results and discussion

MEA was used as the benchmark of our study and aqueous solutions of different concentrations were tested for CO_2 absorption at room temperature (around 25°C) and 40°C. The formation of MEA carbamate was demonstrated by the appearance of carbonyl signal at δ 164.6 ppm. This carbamate carbonyl signal was confirmed by gHMBC 2D NMR spectroscopy which displayed a long range coupling between the carbamate carbonyl carbon atom (C=O) and the proton of the methylene NCH_2 group (figure 1). The carbamate carbonyl resonance increased in intensity and then started to decrease accompanied by the appearance of a new carbonyl resonance at δ 160.8 ppm. The new resonance was assigned to MEA bicarbonate. The carbonyl resonance in this species shows no long range coupling with the methylene NCH_2 protons in the gHMBC 2D NMR spectrum. A stacked quantitative ^{13}C NMR spectra of CO_2 absorption with 4M aqueous MEA at room temperature is shown in figure 2. The speciation with reaction time is clearly demonstrated in the spectra.

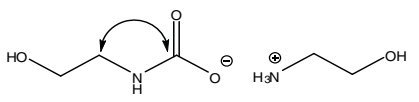

Figure 1: gHMBC 2D NMR relationship of δ 164.6 ppm signal of MEA-H_2O-CO_2

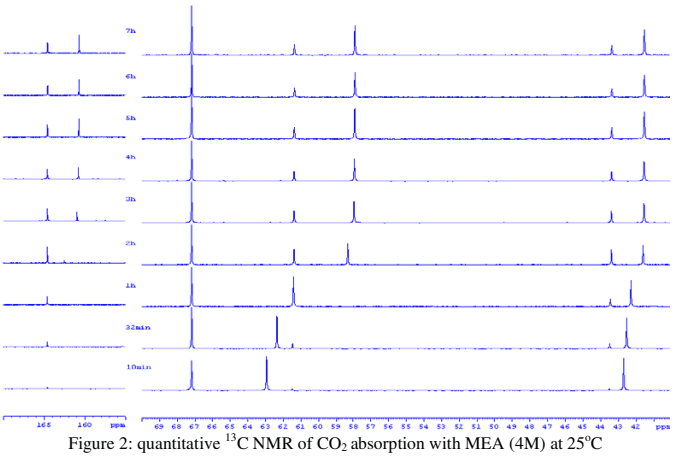

Figure 2: quantitative ^{13}C NMR of CO_2 absorption with MEA (4M) at 25°C

The absorption of CO_2 by aqueous MEA of different concentrations at different temperatures was studied and some results are shown in figure 3. The graphs in figure 3 show that the 2M MEA (3-b, 3-d) has an earlier and sharper turn on the curve of its carbamate than MEA of 4M at the same reaction temperature (3-a, 3-c). MEA of the same concentration reached maximum concentration of carbamate at a similar time (3-a and 3-c; 3-b and 3-d), but the higher reaction temperature caused a faster decomposition of bicarbonate, and hence gave lower concentration of bicarbonate. These results show the influence of concentration and reaction temperature on MEA's CO_2 absorption capacity, and also revealed a clear pathway of speciation with reaction time.

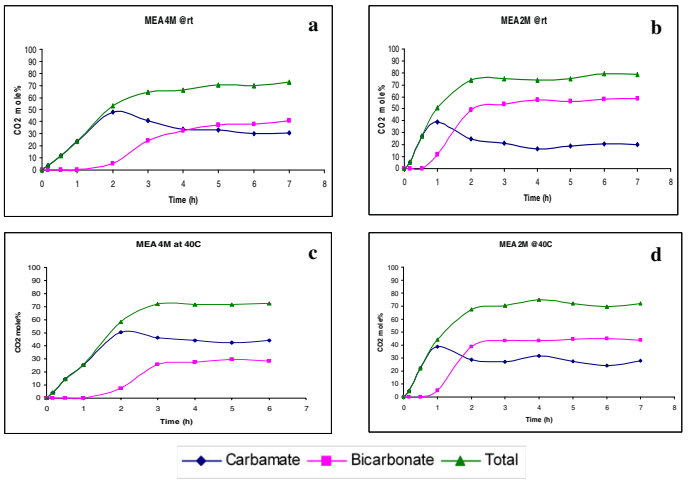

Figure 3: Absorption of CO_2 with MEA (4M and 2M) at room temperature and 40° C

It is important to note that the timescale in our experiments is hours, rather than the minutes that is typical in PCC pilot plants. This is because the absorbing solution is exposed to a low flux of CO_2, rather than the high flux of a PCC absorption column. This is done to permit accurate and reproducible sampling through the course of the reaction.

The absorption of CO_2 by different amines likewise clearly shows their speciation through their ^{13}C NMR spectra. The results of CO_2 absorption at room temperature with 4M solutions of monoethanolamine (MEA), *N*-methyl-ethanolamine (Me-MEA) and *N*-methyl-diethanolamine (Me-DEA) are shown in figure 4. MEA formed the carbamate and converted partially to bicarbonate during the reaction. Me-MEA also formed a carbamate and this

intermediate converted to bicarbonate faster and to a greater extent. Consistent with its structure, the tertiary amine, Me-DEA, could not form carbamate in the reaction and only formed bicarbonate; it also had the highest CO_2 absorbing capacity of the three amines shown here. However, this was also the slowest to react, especially at the beginning of the reaction. The amount of other (unknown) products formed in the CO_2 absorption with MEA and Me-MEA was very small, and their chemical shift (158.4 ppm) was similar to that of 2-oxazolindone [2]. The byproduct formed in Me-DEA reaction needs further study for its identification. All these byproducts released CO_2 in the subsequent desorption experiments.

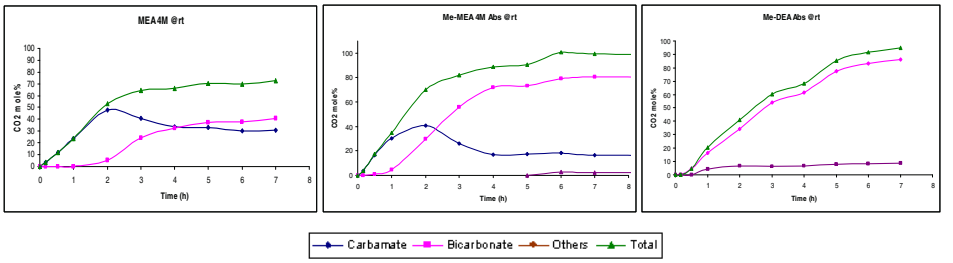

Figure 4: Absorption of CO_2 with MEA (4M), Me-MEA (4M) and Me-DEA (4M) at room temperature

The examples described above illustrate the influence of amine structure on their speciation and total CO_2 absorbing capacity. The following example shows the influence of steric-hindrance of amine structure on amine speciation and CO_2 capture capacity. The CO_2 absorption of a 2M aqueous solution of a sterically-hindered primary amine, 2-amino-2-methyl-propane-1,3-diol (AMPD) was studied at room temperature. The reaction was monitored with the quantitative ^{13}C NMR analysis, and the results showed that the carbamate (δ 164.2 ppm) was formed early in the reaction and then converted rapidly to bicarbonate (see figure 5). When a higher concentration, 4M, was used this amine formed a white precipitate after 1 hour at both room temperature and at 40°C. The formed solid was isolated, then dissolved in water and identified with ^{1}H and quantitative ^{13}C NMR as the amine carbonate, since the ratio of the amine and carbonyl signals was 2 to 1. This carbonate solution displayed the same carbonyl signal as that which appeared in the NMR spectra at 1 hour in figure 5. This suggests that AMPD carbamate quickly converted to a carbonate, as the instability of the carbamate made the conversion happen at the early stage of the reaction and the pH value at this stage favored the formation of carbonate rather than bicarbonate. As this carbonate only exists for a short time in the reaction before transformed to bicarbonate (δ 161.7 ppm), it can be classified as bicarbonate for the purposes of calculation (figure 6). This classification does not affect the analytical results. The curve in figure 6 showed that maximum amount of AMPD carbamate was very low, and was reached at an early stage of the reaction. It had high conversion to bicarbonate, thereby demonstrating a high capacity for CO_2 absorption (106 mole% at 3 hours). It can be expected that this CO_2 rich AMPD solution should perform well in desorption, and that was indeed the case, with a near complete CO_2 release during desorption. These promising results for AMPD suggest that amines with similar structural characteristics should also perform well.

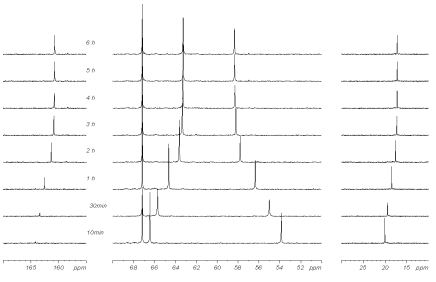

Figure 5: ^{13}C NMR of CO_2 absorption of 2-amino-2- methyl-propane-1,3-diol (2M) at room temperature

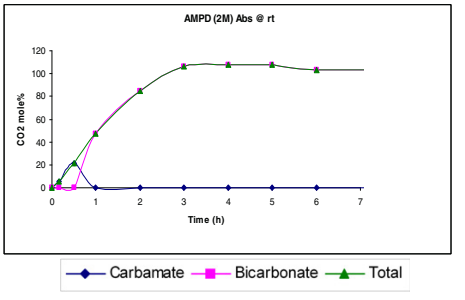

Figure 6: CO_2 absorption of 2-amino-2-methyl- propane-1,3- diol (2M) at room temperature

We have also applied this method to follow the desorption of CO_2 from the CO_2-rich amine solutions generated during the CO_2 absorption process. By measuring the amount of carbonyl carbons with quantitative ^{13}C NMR, the remaining CO_2 can be calculated as a molar percentage, and the species of the molecules which hold the remaining CO_2 as a carbonyl group can also be identified. Hence the total capacity of CO_2 desorption can be obtained and speciation in desorption also observed. The CO_2 desorbing reactions were carried out by heating the CO_2-rich amine solutions in a pear shaped flask in a preheated oil bath of 90°C. At this temperature, most bicarbonate formed in a CO_2 absorption decomposed completely within the first 10 minutes. Examples of CO_2 desorption of MEA, Me-MEA and Me-DEA are shown in figure 7. As expected, both MEA and Me-MEA carbamates are very stable under the desorption conditions used, but Me-DEA released CO_2 faster and to a greater extent due to its higher proportion of bicarbonate formed in the CO_2 absorption step. The results also indicated that both MEA and Me-MEA are able to recapture CO_2 molecules released from bicarbonate decomposition to form more carbamates in desorption step. Although Me-MEA had higher CO_2 absorbing capability (96.2 mole% at 24 hours), it maintained 48.3 mole% of CO_2 at the end of desorption through CO_2 recapture. In comparison MEA retained 55.7 mole% of total CO_2 at the end of desorption. The CO_2 desorption with CO_2 rich Me-DEA was fast and essentially complete as expected. In the future we will lower the CO_2 desorption temperature to reduce the reaction rate and obtain more details about bicarbonate decomposition, in particular the minimum temperature required for bicarbonate decomposition. Lowering the desorption temperature will reduce energy requirements and hence improve the economics of the PCC process.

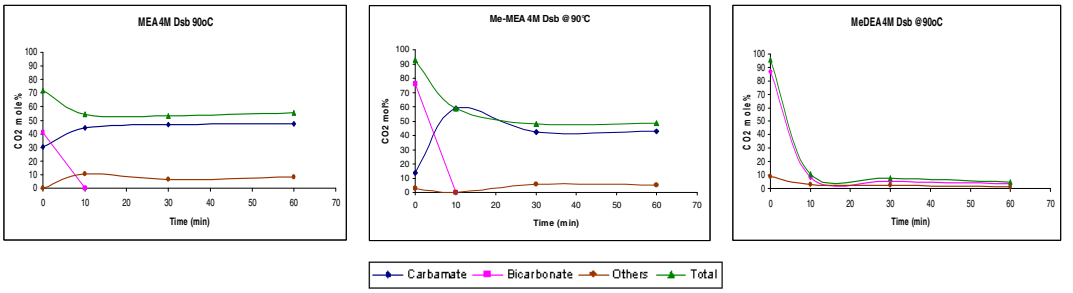

Figure 7: CO_2 desorption of MEA, MMEA and MDEA at 90°C

Piperazine is used as a "promoter" in industry for CO_2 capture and we have applied the quantitative ^{13}C NMR method of our study to its behaviour in CO_2 absorption and desorption. Piperazine was prepared as a 1M aqueous solution and reacted with CO_2 under our standard conditions at room temperature. The reaction was fast and nearly reached the peak CO_2 absorption at 1 hour reaction time. The CO_2 enriched piperazine solution from this absorption was heated with an oil bath at 90°C to strip the CO_2, but still maintained 61% (mole ratio to amine) of CO_2 in the solution after 60 minutes of desorption time.

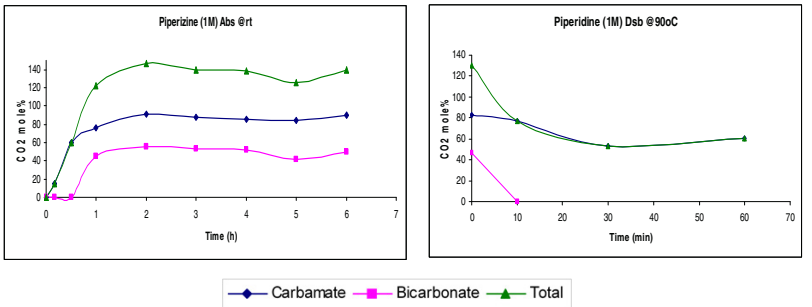

Figure 8: CO_2 absorption and desorption of piperazine (1M)

4. Conclusion

From the above results and discussion, it is clear that the methodology developed in our research is an easy and useful tool to apply to the study of reaction systems of amine-H_2O-CO_2 that does not require any special equipment apart from NMR spectrometers. The application of this method to our study has greatly extended our knowledge about reactions of amines and CO_2 in water solution. We have applied this method of NMR study of CO_2 absorption and desorption to screening a large number of aqueous amines with a wide range of structural diversity, mixed amines of different formulation, and pilot plant samples from absorber and stripper. We have also studied these amines under different reaction conditions including different amine concentrations, reaction temperatures, CO_2 partial pressures, and so on. All of our studies indicate that this method as an easy and reliable tool for investigating amines in PCC, and more results, including kinetic studies, will be forthcoming.

5. Experimental

All the reactions were carried out in standardised reaction apparatus and under standardised conditions as described in Section 2 of this paper. The baths were stabilised at the required temperature before reaction and maintained at the same temperature during reactions. Deionised water was used to make the amine solutions. NMR data were acquired with Bruker-Biospin Av400 NMR spectrometer and processed with Bruker-Biospin Topspin v2.1 software. All the amines were purchased from major chemical commercial suppliers and used without further purification.

5.1 General method of CO_2 absorption with aqueous amine solutions

An amine compound (0.1 mole) was dissolved in water and made up to 25.00 ml in a 25 ml volumetric flask so that the concentration of the amine solution was 4M unless stated otherwise. Lower concentrations of amine, 2M or 1M, were employed when amines of low water solubility were used, or when the amines formed precipitates during CO_2 absorption. The amine solution (15 ml) was added to a 25 ml 2-necked pear shaped flask which was linked or equipped with standard attachments as described in section 2. The solution was maintained in a bath of the required temperature and stirred at 900 rpm for 20 minutes. Carbon dioxide was then bubbled through the solution as described in section 2, and the gas outlet was adjusted to just above the stirring bar so that it did not prevent stable and constant stirring. A reaction sample was taken for NMR analysis at different times. For a convenient comparison, reaction samples were taken at 10 minutes, 30 minutes and 60 minutes, and then at every hour to 6 or 7 hours. Most amines were maintained 24 hours for the absorption reaction to achieve equilibrium.

5.2 General method of CO_2 desorption with CO_2 enriched aqueous amine solutions

To make a quick investigation of desorption, the starting solvent was a CO_2-rich solution obtained from the final solution of absorption at room temperature. Concentration of each species and total CO_2 molar percentage was recorded as the starting point. The final CO_2 enriched aqueous amine solutions obtained from the above absorptions were used without changing the flask. The CO_2 supply tube was removed, and the condenser and ice trap were disconnected to let CO_2 gas in the containers escape, and then reconnected with the reaction flask and the free flask neck was sealed with a stopper. The reaction flask was warmed with a preheated oil bath of 90^{o}C. Release of CO_2 was observed immediately and the samples of the reaction were taken for NMR analysis at 10 minutes, 30 minutes and 60 minutes of reaction time.

The CO_2 desorption can also be performed the day after the absorption stage if the CO_2-rich amine solution is kept in a sealed flask and maintained in a fridge of 4^{o}C.

5.3 General method of NMR analysis

All the reaction samples were taken directly into a 5 mm NMR tube. An external standard of 1,4-dioxane was added to the tube. Proton NMR and quantitative proton decoupled ^{13}C NMR were measured with Bruker-Biospin Av400 without deuterium lock. For most cases, the sample taken at 2 or 3 hours of absorption time were measured

for relaxation time as they contained a high concentration of carbamate and bicarbonate as well as amines. However, this time was adjusted for some of the slower or faster reacting amines as required. The delay time (D1) was chosen to be not less than 5 times the longest relaxation time (T_1) and 32 scans were collected for each sample. The data was processed with Bruker-Biospin Topspin v2.1 software.

5.4 CO_2 absorption with MEA (4M) at room temperature

MEA (6.01 g, 0.1 mole) was dissolved in deionised water and made up to 25.00 ml solution in a volumetric flask. The MEA solution (15 ml) was added to a 50 ml 2-necked pear-shaped flask with standard attachments as described in section 2 and a water bath of 25°C was used to maintain the solvent temperature. CO_2 gas was bubbled to the flask through a Teflon tube (described in section 2). The samples were taken at reaction times of 10min, 30min, 1h, 2h, … 7h and 24 h. An external standard of 1,4-dioxane was added to each NMR sample and all the samples were analysed with quantitative ^{13}C NMR by using the Bruker-Biospin Av400.

5.5 CO_2 desorption from CO_2–enriched MEA at 90^oC

CO_2-rich solution from the end of the above absorption experiment was used for CO_2 desorption with a preheated oil bath (90^oC) as described in the general method. Samples were taken at 10, 30 and 60 minutes of reaction time for quantitative ^{13}C NMR analysis.

Absorption and desorption of other amines were also carried out using the same method with possible adjustment of their concentration. Reaction temperatures were adjusted according to the study plan.

6. Acknowledgement

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